ANALYSIS OF ROTATIONALLY RESOLVED SPECTRA TO NON-DEGENERATE (a_1'') UPPER-STATE VIBRONIC LEVELS IN THE $\tilde{A}^2E'' - \tilde{X}^2A_2'$ ELECTRONIC TRANSITION OF NO_3

MOURAD ROUDJANE, TERRANCE JOSEPH CODD, *Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA*; MING-WEI CHEN, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL, USA*; HENRY TRAN, DMITRY G. MELNIK, TERRY A. MILLER, *Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA*; JOHN F. STANTON, *Department of Chemistry, The University of Texas, Austin, TX, USA*.

The vibronic structure of the $\tilde{A} - \tilde{X}$ electronic spectrum of NO_3 has been observed using both room-temperature and jet-cooled samples. A recent analysis of this structure is consistent with the Jahn-Teller effect (JTE) in the e' ν_3 vibrational mode (N-O stretch) being quite strong while the JTE in the e' ν_4 mode (O-N-O) bend) is rather weak. Electronic structure calculations qualitatively predict these results but the calculated magnitude of the JTE is quantitatively inconsistent with the spectral analysis.

Rotationally resolved spectra have been obtained for over a dozen vibronic bands of the $\tilde{A} - \tilde{X}$ electronic transition in NO_3. An analysis of these spectra should provide considerably more experimental information about the JTE in the $\tilde{A}$ state of NO_3 as the rotational structure should be quite sensitive to the geometric distortion of the molecule due to the JTE. This talk will focus upon the parallel bands, which terminate on $\tilde{A}$ state levels of a_1'' vibronic symmetry, which were the subject of a preliminary analysis reported at this meeting in 2014. We have now recorded the rotational structure of over a half-dozen parallel bands and have completed analysis on the 3_0^1 and $3_0^1 4_0^1$ transitions with several other bands being reasonably well understood. Two general conclusions emerge from this work. (i) All the spectral bands show evidence of perturbations which can reasonably be assumed to result from interactions of the observed $\tilde{A}$ state levels with high vibrational levels of the $\tilde{X}$ state. The perturbations range from severe in some bands to quite modest in others. (ii) Analyses of observed spectra, insofar as the perturbations permit, have all been performed with an oblate symmetric top model including only additional spin-rotation effects. This result is, of course, consistent with an effective, undistorted geometry for NO_3 of D_{3h} symmetry on the rotational timescale.